ELECTRON PAIRING AND CHEMICAL BONDS. PHYSICAL MEANING OF EFFECTIVE PAIRS

Robert PONEC and Filip UHLIK

Institute of Chemical Process Fundamentals,
Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchdol, The Czech Republic

The physical meaning of the so-called effective pairs which have been introduced recently within the formalism of pair population analysis is discussed using the analysis of conditional probabilities of electron density distribution for electron 1 with the reference electron fixed in a certain point 2. It is demonstrated that from the point of view of the mutual coupling of electron motions, the effective pairs behave analogously to singlet pairs. Based on this finding, effective pairs can be interpreted as the fraction of singlet pairs that is directly involved in bonding.

The existence and stability of molecular species is, to considerable extent, conditional on the existence of relatively strong attractive forces between the constituent atoms. Such forces possess some specific properties such as saturation, relatively strict directionality and space localization as well as approximate transferability, which enabled additivity schemes to be set up for various molecular properties. Generalization of the idea of exclusive interatomic interactions with the above specific properties has led to the introduction of one of the most fertile chemical concepts – the concept of the chemical bond.

Because of the immense debt which chemistry owes to this concept, a lot of effort was devoted to the elucidation of the nature of the chemical bond[1]. A fundamental contribution in this respect is due to Lewis[2], whose idea of the chemical bond as a shared electron pair was a major step forward in the rationalization and understanding of the chemical structure, and this success gave it the force of a law. This is perhaps why this idea survived the advent of quantum mechanics with its concept of the delocalized wave function and why a number of studies were aimed at reconciliating the more fundamental quantum description with the qualitative but highly appealing Lewis model[3–31]. The first attempt was based on the concept of the so-called localized orbitals formed from canonical orbitals, resulting from the solution of the Hartree–Fock equations, by unitary transformations according to various criteria[3–11]. Although such orbitals usually correspond quite well to the classical picture of localized chemical bonds, this approach cannot be regarded as completely satisfactory: in fact, because of their

one-electron nature, the localized orbitals are unable to say anything about the role of electron pairs in bonding. The simplest quantity bearing information about the pair behaviour is the so-called pair density[32,33], by means of which the problem of the chemical bond has been analyzed in various studies[20–24,29]. In addition to related earlier studies of various authors[34–36], this problem has also been addressed in our previous study[37] in which a new methodology for the analysis of the pair density based on the idea of Mulliken population analysis was introduced.

Using this approach we were able to demonstrate that properly defined pair populations open an extremely clear and simple way to reproducing the classical structural formula. The fundamental role in this respect is played by the so-called effective pair populations, defined as the difference between singlet and (one-third) triplet pair populations. In spite of their rather speculative definition, the effective pair populations display various important properties associated usually with chemical bonds (approximate transferability, proportionality to the multiplicity of the bond, compatibility with the valence concept[38]).

Our aim in this study is to pursue the results of our previous studied in this field[37,39–41] and to analyze the physical meaning of effective pairs in more detail.

THEORETICAL

Although the basics of the pair population analysis underlying the concept of effective pairs have been described in previous studies[37,40], we consider it appropriate to recapitulate briefly at least some basic concepts to the extent necessary for the purpose of this study.

The (spinless) pair density $\rho(1,2)$ is generally defined by Eq. (1) as a diagonal element of the second order density matrix $\rho(1,2,1',2')$

$$\rho(1,2) = \frac{N(N-1)}{2} \int \Phi^2 d\sigma_1 d\sigma_2 \ldots d\sigma_N dr_3 dr_4 \ldots dr_N \quad , \tag{1}$$

where N is the number of electrons and $d\sigma_i$, dr_j denote the volume elements of the spin and space coordinates of electrons i and j, respectively.

This general definition can be written in the following form:

$$\rho(1,2) = \sum_{\alpha\beta\gamma\delta} \Omega_{\alpha\beta\gamma\delta} \chi_\alpha(1)\chi_\beta(1)\chi_\gamma(2)\chi_\delta(2) \quad . \tag{2}$$

In the SCF approximation, the four-index matrix Ω can be expressed in terms of matrix elements of the conventional charge density–bond order matrix,

$$\Omega_{\alpha\beta\gamma\delta} = \frac{1}{2}\sum_{\alpha\beta}\sum_{\gamma\delta}\left(p_{\alpha\beta}\,p_{\gamma\delta} - \frac{1}{2}\,p_{\alpha\gamma}\,p_{\beta\delta}\right) \quad . \tag{3}$$

As demonstrated in our previous study[37], more convenient than the usual expansion of the pair density in the basis of atomic orbitals (Eq. (2)) is the alternative expansion in the basis of two-electron functions, geminals,

$$\rho(1,2) = \sum_{\alpha\beta}\Gamma_{\alpha\beta}\lambda_\alpha(1,2)\,\lambda_\beta(1,2) \quad . \tag{4}$$

The advantage of this alternative transcription is in the fact that in this case, the pair density has the conventional two-index matrix form similar to the first order density matrix in the basis of orbitals. This allows us to make use of the analogy with the well-known Mulliken population analysis[42] and to introduce pair density population analysis based on dividing the expression $\mathrm{Tr}(\Gamma\Sigma)$, which gives the total number of electron pairs ($N(N-1)/2$), into the mono- and biatomic contributions,

$$\mathrm{Tr}\Gamma\Sigma = \sum_{\alpha\beta}\Gamma_{\alpha\beta}\Sigma_{\beta\alpha} \quad , \tag{5a}$$

$$\Sigma_{\beta\alpha} = \int\lambda_\alpha(1,2)\,\lambda_\beta(1,2)\mathrm{d}r_1\mathrm{d}r_2 \quad , \tag{5b}$$

$$\mathrm{Tr}\Gamma\Sigma = \sum_A\Pi_{AA} + \sum_{A<B}\Pi_{AB} \quad . \tag{5c}$$

In view of the fact that in the geminal pair density expansion the matrix Γ has a special block diagonal form corresponding to the contributions of the singlet and triplet pairs (Eq. 6), the individual mono- and biatomic populations in Eq. (5c) can be further decomposed into contributions from the separate singlet and triplet pairs,

$$\Gamma = \Gamma^{(s)} \oplus \Gamma^{(t)} \quad . \tag{6}$$

Such a decomposition was performed both for a simpler case where the geminal basis is orthogonal and for the general case of a nonorthogonal basis. The corresponding relations can be found in refs[37,41], where we have demonstrated that the crucial role in

the practical application of the proposed population analysis is played by the so-called effective pair populations defined by the following expressions*

$$\Pi_{AA}^{eff} = \Pi_{AA}^{(s)} - \frac{1}{3} \Pi_{AA}^{(t)} \tag{7a}$$

$$\Pi_{AB}^{eff} = \Pi_{AB}^{(s)} - \frac{1}{3} \Pi_{AB}^{(t)} \quad . \tag{7b}$$

Although such a definition seems to be rather speculative at first sight, the effective pair populations prove to be very useful because it is just their values that remarkably correspond to the classical picture of molecular structure represented by the structural formula. This correspondence arises from the fact that the values of biatomic effective populations Π_{AB}^{eff}, which characterize the probability of finding the (effective) electron pair between the atoms A,B, attain nonzero values only between atoms joined by a formal bond in the structural formula, whereas their values are negligible between non-bonded atoms. Moreover, where the effective populations indicate the presence of a bond, the corresponding contributions are virtually independent of the type of the bonded atoms and, rather than on the nature of the bonded atoms, depend on the multiplicity of the bond. Thus, the values for all single bonds, for instance, are close to 0.5, whereas the populations for double and triple bonds are close to 1 and 1.5, respectively.

Another important feature justifying the introduction of effective pair populations is that for a given type of bond, their values are proportional to the experimental bond energies[37] and, also, that they are simply related to the concept of quantum chemical valence[38]. So we can see that the effective population values remarkably reflect many of the attributes which are usually connected with chemical bonds. This intuitive parallel is additionally supported by the interesting normalization condition (8), according to which the sum of all effective pair populations is equal to $N/2$, which is just the number of bonds plus free electron pairs available for a molecule with N valence electrons:

$$\sum_A \Pi_{AA}^{eff} + \sum_{A<B} \Pi_{AB}^{eff} = \frac{N}{2} \quad . \tag{8}$$

* Such a definition of effective populations applies, as demonstrated in ref.[41], only to closed shell molecules with zero net spin or to radicals with one odd electron. For the states of other multiplicity the situation is more complex.

Our aim in this study is to pursue the above parallel and to analyze the possible relation of effective pairs to chemical bonds in more detail. Main attention will be concentrated on the analysis of effective pairs from the point of view of the mutual coupling of electron motions.

Underlying our analysis is the transcription of the well-known expression dividing the pair density into contributions from electrons with parallel and antiparallel spins[22,43],

$$\rho(1,2) = \rho^{\alpha\alpha}(1,2) + \rho^{\alpha\beta}(1,2) \quad . \tag{9}$$

In our case, this separation is written in the alternative form (*10*), where the individual terms correspond to contributions of the spin pure singlet and triplet states of the electron pair,

$$\rho(1,2) = \rho^{(s)}(1,2) + \rho^{(t)}(1,2) \quad . \tag{10}$$

In the case where the pair density is derived from the one-determinantal wave function, the corresponding contributions are given by Eqs (*11*)

$$\rho^{(s)}(1,2) = \frac{1}{8}\,\rho(1)\,\rho(2) + \frac{1}{8}\,\rho_1^2(1,2) \quad , \tag{11a}$$

$$\rho^{(t)}(1,2) = \frac{3}{8}\,\rho(1)\,\rho(2) - \frac{3}{8}\,\rho_1^2(1,2) \quad , \tag{11b}$$

where $\rho(1)$ and $\rho_1^2(1,2)$ are the diagonal and nondiagonal elements of the conventional first order density matrix, defined by Eqs (*12*):

$$\rho(1) = 2 \sum_i^{\text{occ}} \varphi_i^2(1) \quad , \tag{12a}$$

$$\rho_1(1,2) = 2 \sum_i^{\text{occ}} \varphi_i(1)\,\varphi_i(2) \quad . \tag{12b}$$

Based on Eqs (*11a*) and (*11b*), the effective pair density is

$$\rho^{\text{eff}}(1,2) = \rho^{(s)}(1,2) - \frac{1}{3}\,\rho^{(t)}(1,2) = \frac{1}{4}\,\rho_1^2(1,2) \quad . \tag{13}$$

The following analysis of the correlation behavior of singlet, triplet and effective pairs is based on the analogy with the analysis which is based on expansion (*9*). Such analysis has been thoroughly discussed in refs[37,43]. The well-known fact that only electrons with parallel spins are correlated in this case (Fermi correlation) whereas electrons with opposite spins are entirely independent, is physically reflected in expressions (*14a*) and (*14b*):

$$\frac{\int \rho^{\alpha\alpha}(1,2)\mathrm{d}r_1}{\frac{1}{2}\,\rho(2)} - \frac{1}{2}\int \rho(1)\mathrm{d}r_1 = -1 \quad , \tag{14a}$$

$$\frac{\int \rho^{\alpha\beta}(1,2)\mathrm{d}r_1}{\frac{1}{2}\,\rho(2)} - \frac{1}{2}\int \rho(1)\mathrm{d}r_1 = 0 \quad . \tag{14b}$$

If the procedure used in deriving the above expressions is applied to the expansion (*10*), the following equations result:

$$\frac{\int \rho^{(t)}(1,2)\mathrm{d}r_1}{\frac{3}{4}\,\rho(2)} - \frac{1}{2}\int \rho(1)\mathrm{d}r_1 = -1 \quad , \tag{15a}$$

$$\frac{\int \rho^{(s)}(1,2)\mathrm{d}r_1}{\frac{1}{4}\,\rho(2)} - \frac{1}{2}\int \rho(1)\mathrm{d}r_1 = +1 \quad , \tag{15b}$$

$$\frac{\int \rho^{\text{eff}}(1,2)\mathrm{d}r_1}{\frac{1}{2}\,\rho(2)} = +1 \quad . \tag{15c}$$

This is a very interesting result. First, triplet pairs are correlated in exactly the same way as the pairs described by the density $\rho^{\alpha\alpha}(1,2)$ (Fermi correlation). This is quite natural, since – apart from the unimportant numerical factor (1/8 instead of 1/4) – the expressions for $\rho^{\alpha\alpha}(1,2)$ and $\rho^{(t)}(1,2)$ are identical. The above parallel, however, does not hold for electrons with opposite spins since, in contrast to the independence of the electron pair described by the pair density $\rho^{\alpha\beta}(1,2)$, the spin pure singlet pairs are coupled and the nature of this coupling is completely opposite to the coupling of triplet pairs. The same coupling then holds, on the basis of Eq. (*15*), also for effective pairs. The parallel between the mutual coupling of singlet and effective pairs is very important. In fact, within the framework of the VB method, the existence of stable chemical bonds is connected with singlet electron pairs, and so the introduction of effective pairs

in pair population analysis can seem to violate the VB model. The above parallel between effective and singlet pairs thus partly solves the problem. The parallel between singlet and effective pairs has some additional interesting consequences. First, since the total number of electron pairs is a sum of singlet and triplet pairs only (Eq. (16)), the effective pairs are nothing else but a certain subset of the whole set of singlet pairs,

$$N^{\text{tot}} = \frac{N(N-1)}{2} = N^{(s)} + N^{(t)} \quad . \tag{16}$$

The rationale behind the exclusion of effective pairs from the whole set of singlet pairs is that the number of singlet pairs ($N(N+2)/8$) is, except for $N = 2$, higher than the number of available bonds and free pairs, and so it is clear that only part of them can participate in the formation of the bonds. The introduction of effective pairs thus only reflects this necessity to separate from the whole set of singlet pairs that part which actively participates in bonding, and effective pairs are thus nothing else but this certain, specifically excluded subset of singlet pairs. The above parallel between the effective pairs and chemical bonds can also be quite convincingly demonstrated by the analysis of conditional probabilities of finding electron 1 at point r_1 with the reference electron 2 fixed at point r_2. These probabilities are given by Eqs ($17a$) – ($17c$) and their graphical visualisation for the molecules of N_2 and H_2O are presented in Figs 1 – 6.

$$P^{(t)}(1) = \frac{\rho^{(t)}(1,2)}{\frac{3}{4}\rho(2)} = \frac{1}{2}\rho(1) - \frac{\rho_1^2(1,2)}{2\rho(2)} \tag{17a}$$

$$P^{(s)}(1) = \frac{\rho^{(s)}(1,2)}{\frac{1}{2}\rho(2)} = \frac{1}{2}\rho(1) + \frac{\rho_1^2(1,2)}{2\rho(2)} \tag{17b}$$

$$P^{\text{eff}}(1) = \frac{\rho^{\text{eff}}(1,2)}{\frac{1}{2}\rho(2)} = \frac{\rho_1^2(1,2)}{4\rho(2)} \tag{17c}$$

The quantities required were generated by conventional *ab initio* calculations using the GAUSSIAN-92 series of programs[44]. Because of the model nature of this study, the calculations were performed in the minimal STO-3G basis set.

RESULTS AND DISCUSSION

Let us discuss the main conclusions resulting from the corresponding figures, first for the case of the N_2 molecule. The resulting cuts of conditional probabilities for singlet, triplet and effective pairs in a plane containing the two nuclei are shown in Figs 1, 2 and 3, respectively. In all cases the reference electron was fixed in the centre of the N≡N
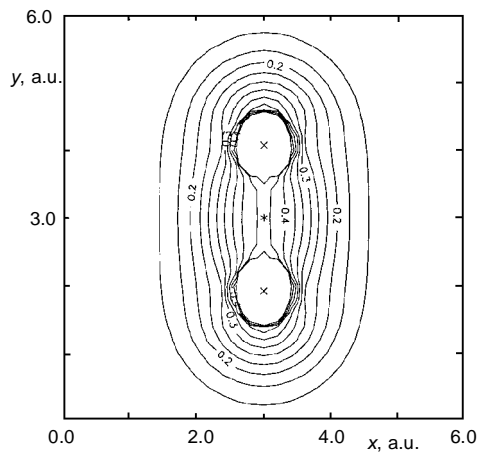
FIG. 1

Conditional probability $P^{(s)}(1)$ of finding electron 1 in a plane containing both nuclei in the N_2 molecule with the singlet paired reference electron 2 localized in the middle of the N≡N bond
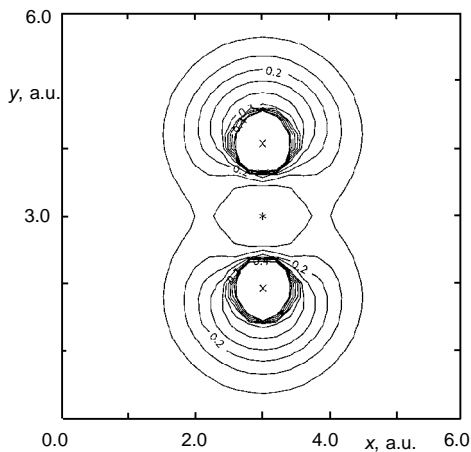

FIG. 2

Conditional probability $P^{(t)}(1)$ of finding electron 1 in a plane containing both nuclei in N_2 with the triplet paired reference electron 2 localized in the middle of the N≡N bond
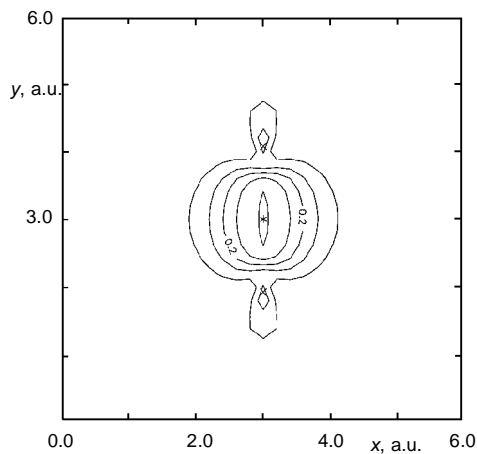

FIG. 3

Conditional effective pair probability $P^{eff}(1)$ of finding electron 1 in a plane containing both nuclei in N_2 with the reference electron 2 localized in the middle of the N≡N bond
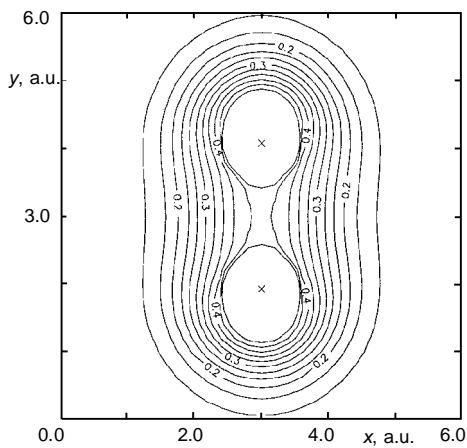

FIG. 4

Total electron density $\rho(1)$ in a plane containing both nuclei in N_2

bond. The analogous cut of the total electron density $\rho(1)$ is shown in Fig. 4. The simplest situation is in the case of triplet pairs, where Fig. 2 clearly demonstrates that if the reference electron is fixed in a certain point (in the middle of the bond in our case), the probability of finding the other electron in the vicinity of the reference point is strongly reduced. This result thus nicely documents the effect of Fermi correlation. On the other hand, the analogous Fig. 1 for singlet pairs suggests that the probability of finding electron 1 in the vicinity of reference electron 2 is increased. This increase is due to the presence of the non-negative term whose presence, as can be seen from Eq. (*17b*), contributes to the accumulation of electron density over the value given by the simple electron density $\rho(1)$ (see Fig. 4 for a comparison). The isolated additional term which corresponds to effective pairs is then shown in Fig. 3. As can be seen from this figure, the probability of finding electron 1 in the vicinity of the reference electron is again increased, hence the corresponding "effective" pair, strongly localized between the atoms, corresponds quite well with the classical Lewis idea of the bond as a shared electron pair.

A similar result confirming the effect of Fermi correlation for triplet pairs as well as the electron density accumulation in the vicinity of the reference electron for singlet and effective pairs is also observed for the H_2O molecule. Figures 5 – 7 display the cuts of the conditional probabilities (*17a*) – (*17c*) in the plane of the molecule. Since our interest was mainly concentrated on the OH bonds, the reference electron was fixed in
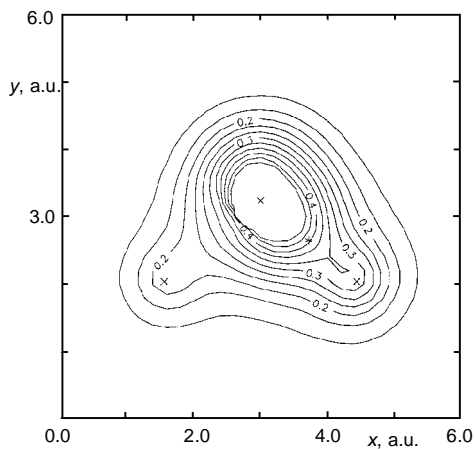

Fig. 5

Conditional probability $P^{(s)}(1)$ of finding electron 1 in the plane containing the nuclei of the H_2O molecule with the singlet paired reference electron 2 localized in the middle of the right O–H bond
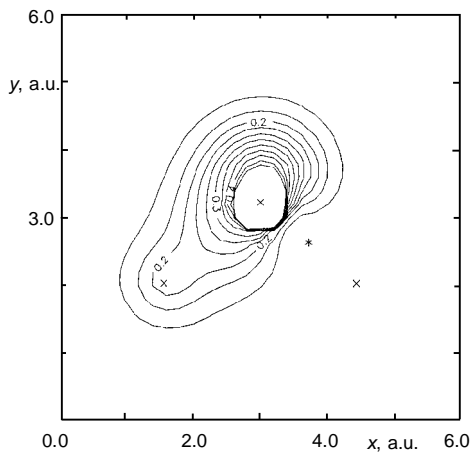

Fig. 6

Conditional probability $P^{(t)}$ of finding electron 1 in the plane containing the nuclei in H_2O with the triplet paired reference electron 2 localized in the middle of the right O–H bond

the centre of one of these bonds. Actually, the choice of the position of the reference electron is quite arbitrary and an alternative point, such as the Bader's critical point on the bond path[45], would also be a feasible choice. Since, however, our calculations gave evidence that the resulting picture of the conditional probabilities is rather insensitive to the precise position of the reference electron (unless its position exceeds certain limits), we confined ourselves to the situation where the critical point is in the centre of the O–H$_1$ bond. From among the results shown in Figs 5 – 7, the case of triplet pairs is worth mentioning (Fig. 6): if the reference electron is placed in the centre of one of the OH bonds, the probability of the other electron being found in the region of that bond is strongly reduced and this electron is predominantly localized in the region of the other O–H bond. This result is very interesting since it agrees well with the conclusions of the classical study by Lennard-Jones[30], according to which the maximum probability of finding two electrons with parallel spins is localized on axes directed to the corners of a tetrahedron. After demonstration of the effect of Fermi correlation on the triplet pair distribution, it is useful to analyze the conditional probabilities for singlet and effective pairs as well. The resulting picture is shown in Figs 5 and 7. Parallel to what was found for N$_2$, a net increase in the accumulation of electron density in the vicinity of the reference electron is observed.

CONCLUSIONS

The physical meaning of the concept of effective pairs introduced previously was analyzed by separating the pair densities into contributions of the singlet and triplet pairs. It is shown that from the point of view of the mutual coupling of electron motions, the effective pairs behave analogously to singlet pairs and actually correspond to the fraction of singlet pairs actively engaged in the formation of bonds. In this study, the for-
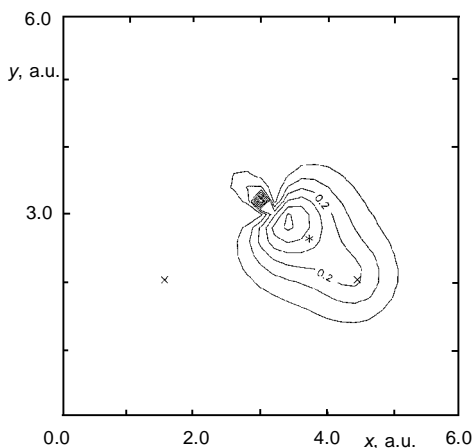

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Conditional effective pair probability $P^{eff}(1)$ of finding electron 1 in the plane containing the nuclei in H$_2$O with the reference electron 2 localized in the middle of the right O–H bond

malism used was only formulated for the simplest SCF approximation, but generalization to correlated wave functions is also possible. Such generalizations are being currently studied in our laboratory and the results will be presented.

REFERENCES

1. Pauling L.: *The Nature of Chemical Bond*. Cornell University Press, Ithaca, New York 1960.
2. Lewis G. N.: J. Am. Chem. Soc. *38*, 762 (1916).
3. Coulson C. A.: Trans. Faraday Soc. *38*, 433 (1942).
4. Lennard-Jones J. E.: Proc. R. Soc. London, A *198*, 14 (1949).
5. Foster J. M., Boys S. F.: Rev. Mod. Phys. *32*, 300 (1960).
6. Edmiston C., Ruedenberg K.: J. Chem. Phys. *43*, S97 (1965).
7. Polak R.: Theor. Chim. Acta *14*, 163 (1969).
8. von Niessen W.: J. Chem. Phys. *56*, 4290 (1972).
9. Magnasco V., Perico A.: J. Chem. Phys. *47*, 738 (1972).
10. Pipek J., Mezey P. G.: J. Chem. Phys. *90*, 4916 (1989).
11. Millie P., Levy B., Berthier G. in: *Localization and Delocalization in Quantum Chemistry* (O. Chalvet, R. Daudel, S. Diner and J. P. Malrieu, Eds), Vol. I. D. Reidel, Dordrecht 1975.
12. Berlin T.: J. Chem. Phys. *19*, 208 (1951).
13. Silberbach H.: J. Chem. Phys. *94*, 2977 (1991).
14. Ruedenberg K.: Rev. Mod. Phys. *14*, 326 (1962).
15. Daudel R., Odiot S., Brion H.: J. Chim. Phys. *51*, 74 (1954).
16. Brion H., Daudel R., Odiot S.: J. Chim. Phys. *51*, 358 (1954).
17. Odiot S., Daudel R.: J. Chim. Phys. *51*, 361 (1954).
18. Brion H., Daudel R., Odiot S.: J. Chim. Phys. *51*, 553 (1954).
19. Aslangul C., Constanciel R., Daudel R., Esnault L., Ludena E. V.: Int. J. Quantum Chem. *8*, 499 (1974).
20. Constanciel R., Daudel R., Gallais F.: C. R. Acad. Sci., 2 *292*, 1387 (1981).
21. Daudel R., Bader R. F. W., Stephens M. E., Borrett D. S.: Can. J. Chem. *52*, 1310 (1974).
22. Bader R. F. W., Stephens M. E.: J. Am. Chem. Soc. *97*, 7391 (1975).
23. Mel Levy B.: J. Am. Chem. Soc. *98*, 6849 (1976).
24. Julg A., Julg P.: Int. J. Quantum Chem. *13*, 483 (1978).
25. Savin A., Becke D. A., Flad J., Mesper J., Preuss H.: Angew. Chem., Int. Ed. Engl. *30*, 404 (1991).
26. Cooper D. L., Gerratt J., Raimondi M.: Chem. Rev. *91*, 929 (1991).
27. Cooper D. L., Gerratt J., Raimondi M. in: *Ab initio Methods in Quantum Chemistry* (K. P. Lawley, Ed.). Wiley, New York 1987.
28. Salem L.: Nouv. J. Chim. *2*, 559 (1978).
29. Leroy G., Peters D., Deplus A., Tihange M.: Nouv. J. Chim. *3*, 213 (1979).
30. Lennard-Jones J. E.: J. Chem. Phys. *20*, 1024 (1952).
31. Bader R. F. W.: Acc. Chem. Res. *8*, 34 (1975).
32. Lowdin P. O.: Phys. Rev. *97*, 1474 (1955).
33. McWeeny R.: Rev. Mod. Phys. *32*, 335 (1960).
34. Karafiloglou P.: Chem. Phys. *128*, 373 (1990).
35. Karafiloglou P.: Chem. Phys. *140*, 373 (1990).
36. Bochicchio R. C.: Theochem, J. Mol. Struct. *228*, 209 (1991).
37. Ponec R., Strnad M.: Int. J. Quantum Chem. *50*, 43 (1994).

38. Gopinathan M. S., Jug K.: Theor. Chim. Acta *63*, 497, 511 (1983).
39. Ponec R.: Croat. Chim. Acta, in press.
40. Ponec R.: Collect. Czech. Chem. Commun. *59*, 505 (1994).
41. Cooper D. L., Ponec R., Thorsteinsson T., Raos G.: Int. J. Quantum Chem., submitted.
42. Mulliken R. S.: J. Chem. Phys. *23*, 1833 (1955).
43. McWeeny R.: *Molecular Quantum Mechanics*, Chapter 5. Academic Press, London 1992.
44. Frisch M. J., Trucks G. W., Head-Gordon M., Gill P. M. W., Wong M. W., Foresman J. B., Johnson B. G., Schlegel H. B., Robb M. A., Reploge E. S., Gomperts R., Anders J. L., Raghavachari K., Binkley J. S., Gonzales C., Martin R. L., Fox D. J., Defrees D. J., Baker J., Stewart J. J. P., Pople J. A.: GAUSSIAN-92 Revision C, Gaussian Inc., Pittsburgh, PA 1992.
45. Bader R. F. W.: Chem. Rev. *91*, 893 (1991).

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